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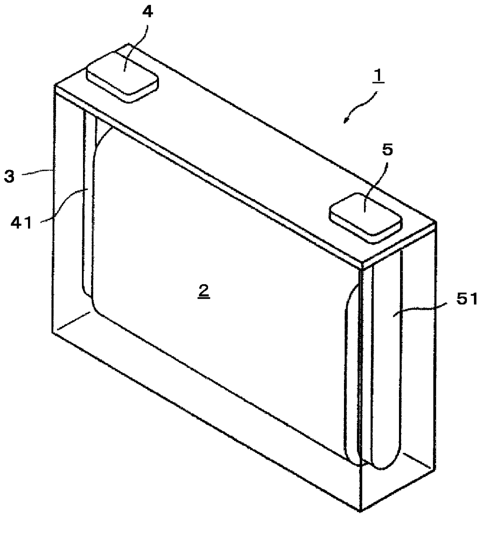
(54) NON-AQUEOUS ELECTROLYTE POWER STORAGE ELEMENT

(57) A nonaqueous electrolyte energy storage device according to one aspect of the present invention includes a positive electrode containing a positive active material containing a tungsten element and a negative electrode containing solid graphite.

Fig. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a nonaqueous electrolyte energy storage device.

BACKGROUND ART

[0002] Nonaqueous electrolyte secondary batteries typified by lithium ion secondary batteries are often used for electronic devices such as personal computers and communication terminals, motor vehicles, and the like, because the batteries are high in energy density. The nonaqueous electrolyte secondary batteries generally include a pair of electrodes electrically separated from each other by a separator, and a nonaqueous electrolyte interposed between the electrodes, and are configured to allow charge transport ions to be transferred between the two electrodes for charge-discharge. In addition, capacitors such as lithium ion capacitors and electric double-layer capacitors are also widely in use as nonaqueous electrolyte energy storage devices other than the nonaqueous electrolyte secondary batteries.

[0003] As a positive active material for a nonaqueous electrolyte energy storage device, a lithium transition metal composite oxide, a polyanion compound or the like is used. In order to improve the performance of the nonaqueous electrolyte energy storage device, or the like, for example, the surfaces of the particles of the positive active material are coated with another compound. Patent Document 1 describes a positive electrode material for a lithium secondary battery in which a particle surface of a lithium-manganese composite oxide is coated with a metal oxide such as titanium oxide or tin oxide. On the other hand, for negative active materials, carbon materials such as graphite have been widely used (see Patent Document 2).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004]

Patent Document 1: JP-A-2001-6676
Patent Document 2: JP-A-2005-222933

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] It is desirable that the nonaqueous electrolyte energy storage device has a large input at the initial stage, and the input is hardly reduced even after the nonaqueous electrolyte energy storage device is stored in a high temperature environment. The input refers to energy (power: W) that can be taken in per unit time by the nonaqueous electrolyte energy storage device during charging. In other words, the input is input power during charging.

[0006] An object of the present invention is to provide a nonaqueous electrolyte energy storage device having a large input at the initial stage and after storage in a high temperature environment.

MEANS FOR SOLVING THE PROBLEMS

[0007] A nonaqueous electrolyte energy storage device according to one aspect of the present invention includes a positive electrode containing a positive active material containing a tungsten element and a negative electrode containing solid graphite.

ADVANTAGES OF THE INVENTION

[0008] According to one aspect of the present invention, it is possible to provide a nonaqueous electrolyte energy storage device having a large input at the initial stage and after storage in a high temperature environment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Fig. 1 is a see-through perspective view illustrating an embodiment of a nonaqueous electrolyte energy storage device.

Fig. 2 is a schematic diagram illustrating an embodiment of an energy storage apparatus including a plurality of nonaqueous electrolyte energy storage devices.

MODE FOR CARRYING OUT THE INVENTION

[0010] First, the outline of a nonaqueous electrolyte energy storage device disclosed in the present specification will be described.

[0011]

[1]: A nonaqueous electrolyte energy storage device according to one aspect of the present invention includes a positive electrode containing a positive active material containing a tungsten element and a negative electrode containing solid graphite.

[0012] The nonaqueous electrolyte energy storage device according to the above [1] has a large input at the initial stage and after storage in a high temperature environment. The reasons therefor are not clear, but the following reasons are presumed. By using the positive active material containing a tungsten element, the resistance of the positive electrode decreases, and the initial input of the nonaqueous electrolyte energy storage device increases. However, when the nonaqueous electrolyte energy storage device is stored in a high temperature environment, the tungsten element contained in the positive active material is eluted into the nonaqueous electrolyte. The eluted tungsten element deposits on the negative electrode, which causes an increase in resistance of the negative electrode. As a result, the input of the nonaqueous electrolyte energy storage device decreases. In particular, when the tungsten element is deposited inside the negative active material particles, it is considered that the resistance further increases and the input decreases. Therefore, it is considered that when solid graphite having few voids therein is used as the negative active material, the tungsten element eluted from the positive active material is suppressed from depositing inside the graphite particles, so that the resistance of the negative electrode is suppressed from increasing. For this reason, according to the nonaqueous electrolyte energy storage device according to the above [1], it is presumed that the input at the initial stage and after storage in a high temperature environment is large.

[0013] The "solid" of the solid graphite means that the inside of the particle of the graphite is filled substantially without voids. More specifically, being "solid" means that in a cross section of a particle observed in a SEM image acquired with the use of a scanning electron microscope (SEM), the ratio of the area of voids (porosity) in the particles to the total area of the particles is 2% or less.

[0014] "The ratio of the area of voids (porosity) in the particles to the total area of the particles" in the graphite particles can be determined by the following procedure.

(1) Preparation of sample for measurement

[0015] The negative electrode to be measured is fixed with a thermosetting resin. A cross section polisher is used to expose a cross section of the negative electrode fixed with the resin to prepare a sample for measurement. It is to be noted that the negative electrode to be measured are prepared in accordance with the following procedure. When the negative electrode before assembling the nonaqueous electrolyte energy storage device can be prepared, the negative electrode is used as it is. In the case of preparing from the assembled nonaqueous electrolyte energy storage device, first, the nonaqueous electrolyte energy storage device is subjected to constant current discharge at a current of 0.1 C to an end-of-discharge voltage under normal usage, into a discharged state. The nonaqueous electrolyte energy storage device in the discharged state is disassembled, and the negative electrode is taken out. A half cell using the taken-out negative electrode as a working electrode and metal Li as a counter electrode is assembled. When the open circuit voltage in this half cell is less than 0.6 V, the half cell is discharged at a current of 0.1 C so that the open circuit voltage is 0.6 V or more. The discharge in the half cell refers to an oxidation reaction in which charge transport ions are released from graphite as a negative active material. The half cell is disassembled, and the negative electrode is taken out, sufficiently washed with dimethyl carbonate, and then dried under reduced pressure at room temperature. The operations from the disassembly of the nonaqueous electrolyte energy storage device to the preparation of the negative electrode to be measured are performed in a dry air atmosphere with a dew point of -40°C or lower. Here, the term "normal use" means use of the nonaqueous electrolyte energy storage device under the charge-discharge conditions recommended or specified for the nonaqueous electrolyte energy storage device.

(2) Acquisition of SEM image

[0016] For acquiring an SEM image, JSM-7001F (manufactured by JEOL Ltd.) is used as a scanning electron microscope. For the SEM image, a secondary electron image is observed. The acceleration voltage is 15 kV. The observation magnification is set such that the number of graphite particles appearing in one field of view is three or more and fifteen or less. The obtained SEM image is stored as an image file. In addition, various conditions such as a spot diameter, a working distance, an irradiation current, luminance, and a focus are appropriately set so as to make the contours of the graphite particles clear.

(3) Cut-out of contour of graphite particle

[0017] The contour of the graphite particle is cut out from the acquired SEM image by using an image cutting function of image editing software Adobe Photoshop Elements 11. The contour is cut out by using a quick selection tool to select the outside of the contour of the graphite particle and edit the part excluding the graphite particle to a black background. In this regard, when the number of graphite particles from which the contours have been able to be cut out is less than three, an SEM image is acquired again, and the cut-out is performed until the number of graphite particles from which the contours have been able to be cut out is three or more.

(4) Binarization processing

[0018] The image of the first graphite particle among the cut-out graphite particles is subjected to binarization processing with, as a threshold value, a concentration set to be 20% lower than the concentration at which the intensity reaches the maximum, with the use of image analysis software PopImaging 6.00. By the binarization processing, the area on the higher-concentration side is calculated as an "area S 1 of voids in the particle".

[0019] Then, the image of the same first graphite particle is subjected to binarization processing with a concentration of 10% as a threshold value. The outer edge of the graphite particle is determined by the binarization processing, and the area inside the outer edge is calculated as a "total area S0 of the particles".

[0020] The ratio (S 1/S0) of S1 to S0 is calculated with the use of S1 and S0 calculated above to calculate a "ratio R1 of the area of voids in the particle to the total area of the particles" in the first graphite particle.

[0021] The images of the second and subsequent graphite particles among the cut-out graphite particles are also each subjected to the binarization processing mentioned above, and the areas S1 and S0 are calculated. Based on the calculated area S1 and area S0, ratios R2, R3, ... of the area of voids of the respective graphite particles are calculated.

(5) Determination of ratio of area of voids

[0022] The average value for all of the ratios R1, R2, R3, ... of the area of voids calculated by the binarization processing is calculated to determine "the ratio of the area of voids (porosity) in the particles to the total area of the particles".

[0023] It is to be noted that, instead of the scanning electron microscope used for "acquisition of SEM image", the image editing software used for "cut-out of contour of graphite particle", and the image analysis software used for the "binarization processing", apparatuses, software, and the like capable of the corresponding measurement, image editing, and image analysis may be used.

[0024] The "graphite" refers to a carbon material in which the average lattice spacing (d_{002}) of a (002) plane determined by an X-ray diffraction method before charge-discharge or in a discharged state is 0.33 nm or more and less than 0.34 nm. In this regard, the "discharged state" of the carbon material means a state discharged such that lithium ions that can be occluded and released in association with charge-discharge are sufficiently released from the carbon material that is a negative active material. For example, the "discharged state" refers to a state where the open circuit voltage is 0.6 V or higher in a half cell that has, as a working electrode, a negative electrode including a carbon material as a negative active material, and has metal Li as a counter electrode.

[0025] [2]: In the nonaqueous electrolyte energy storage device according to the above [1], the negative electrode may have a negative active material layer containing the solid graphite, and the negative active material layer may have a porosity of 40% or more. The negative active material layer having a porosity of less than 40% is usually formed by consolidation by pressing or the like. When the pressing pressure is strong, the solid graphite particles crack, and the surface area of the solid graphite increases, so that the tungsten element is more deposited on the surface of the solid graphite after storage in a high temperature environment, the resistance further increases and the input tends to decrease. On the other hand, in the negative active material layer having a porosity of 40% or more, the number of cracks of the solid graphite particles is small, and according to the nonaqueous electrolyte energy storage device according to the above [2], the input after storage in a high temperature environment tends to further increase.

[0026] The "porosity (%)" of the negative active material layer is determined by a calculation formula of $(1 - V_2/V_1) \times 100$, where an apparent volume (volume including voids) of the negative active material layer is defined as V_1 and a sum of actual volumes of materials constituting the negative active material layer is defined as V_2. The sum V_2 of actual volumes of the materials constituting the negative active material layer can be calculated from the content of each material in the negative active material layer and the true density of each material.

[0027]

[3]: In the nonaqueous electrolyte energy storage device according to the above [1] or [2], the positive active material further may contain a transition metal element other than the tungsten element, and a content of the tungsten element with respect to a transition metal element other than the tungsten element in the positive active material may be 0.2 mol% or more. According to the nonaqueous electrolyte energy storage device according to the above [3], since a sufficient amount of tungsten element is contained in the positive active material, the input of the nonaqueous electrolyte energy storage device at the initial stage and after storage in a high temperature environment further increases.

[4]: In the nonaqueous electrolyte energy storage device according to any one of the above [1] to [3], the solid graphite may be solid natural graphite. Natural graphite has higher crystallinity than artificial graphite. Therefore, when the solid graphite is solid natural graphite, the discharge capacity per mass of the negative active material increases, and according to the nonaqueous electrolyte energy storage device according to the above [4], the input at the initial stage and after storage in a high temperature environment also further increases.

[5]: In the nonaqueous electrolyte energy storage device according to any one of the above [1] to [4], the solid graphite may have an average particle size of 5 pm or more. When solid graphite having a large particle size is used, the surface area of the solid graphite is reduced, so that deposition of tungsten element on the surface of the solid graphite is less likely to occur, and according to the nonaqueous electrolyte energy storage device according to the above [5], the input after storage in a high temperature environment further increases.

[0028] The "average particle size" means a value at which a volume-based integrated distribution calculated in accordance with JIS-Z-8819-2 (2001) is 50% based on a particle size distribution measured by a laser diffraction/scattering method for a diluted solution obtained by diluting particles with a solvent in accordance with JIS-Z-8825 (2013).

[0029] A nonaqueous electrolyte energy storage device, an energy storage apparatus, and a method for manufacturing a nonaqueous electrolyte energy storage device according to an embodiment of the present invention, and other embodiments will be described in detail. The names of the respective constituent members (respective constituent elements) for use in the respective embodiments may be different from the names of the respective constituent members (respective elements) for use in the background art.

<Nonaqueous electrolyte energy storage device>

[0030] A nonaqueous electrolyte energy storage device according to an embodiment of the present invention (hereinafter, also referred to simply as an "energy storage device") includes: an electrode assembly including a positive electrode, a negative electrode, and a separator; a nonaqueous electrolyte; and a case that houses the electrode assembly and the nonaqueous electrolyte. The electrode assembly is typically a stacked type obtained by stacking a plurality of positive electrodes and a plurality of negative electrodes with separators interposed therebetween, or a wound type obtained by winding a positive electrode and a negative electrode stacked with a separator interposed therebetween. The nonaqueous electrolyte is present with the positive electrode, negative electrode, and separator impregnated with the electrolyte. A nonaqueous electrolyte secondary battery (hereinafter, also referred to simply as a "secondary battery") will be described as an example of the nonaqueous electrolyte energy storage device.

(Positive electrode)

[0031] The positive electrode has a positive substrate and a positive active material layer disposed directly on the positive substrate or over the positive substrate with an intermediate layer interposed therebetween.

[0032] The positive substrate has conductivity. Whether the positive substrate has "conductivity" or not is determined with the volume resistivity of 10^7 Ω cm measured in accordance with JIS-H-0505 (1975) as a threshold. As the material of the positive substrate, a metal such as aluminum, titanium, tantalum, or stainless steel, or an alloy thereof is used. Among these metals and alloys, aluminum or an aluminum alloy is preferable from the viewpoints of electric potential resistance, high conductivity, and cost. Examples of the positive substrate include a foil, a deposited film, a mesh, and a porous material, and a foil is preferable from the viewpoint of cost. Accordingly, the positive substrate is preferably an aluminum foil or an aluminum alloy foil. Examples of the aluminum or aluminum alloy include A1085, A3003, A1N30, and the like specified in JIS-H-4000 (2014) or JIS-H-4160 (2006).

[0033] The average thickness of the positive electrode substrate is preferably 3 pm or more and 50 pm or less, more preferably 5 pm or more and 40 pm or less, still more preferably 8 pm or more and 30 pm or less, and particularly preferably 10 pm or more and 25 pm or less. By setting the average thickness of the positive substrate to the above range, it is possible to enhance the energy density per volume of a secondary battery while increasing the strength of the positive substrate.

[0034] The intermediate layer is a layer arranged between the positive electrode substrate and the positive active material layer. The intermediate layer includes a conductive agent such as carbon particles, thereby reducing contact resistance between the positive substrate and the positive active material layer. The configuration of the intermediate layer is not particularly limited, and includes, for example, a binder and a conductive agent.

[0035] The positive active material layer includes a positive active material. The positive active material layer contains optional components such as a conductive agent, a binder (binding agent), a thickener, a filler, or the like as necessary.

[0036] The positive active material contains a tungsten element. This tungsten element may be present, for example, in the form of a compound such as an oxide (WO_3). The compound containing a tungsten element covers at least a part of the surface of particles of a substance capable of occluding and releasing charge transport ions such as lithium ions, for example. In other words, the positive active material may contain a substance capable of occluding and releasing charge transport ions and a compound containing a tungsten element. The positive active material may be substantially composed only of a substance capable of occluding and releasing charge transport ions and a compound containing a tungsten element. The substance capable of occluding and releasing charge transport ions itself may contain a tungsten element. The tungsten element may be present, for example, on the surfaces of the particles of the positive active material. The tungsten element may be present inside the particles of the positive active material. As described above, when the positive active material contains a tungsten element, side reactions in the positive electrode can be suppressed, and conductivity of charge transport ions such as lithium ions can be improved. As a result, the input of the nonaqueous electrolyte energy storage device can be improved. As a form in which a tungsten element is contained in the positive active material, there is a form in which a compound containing a tungsten element is coated on a particle surface of a substance capable of occluding and releasing charge transport ions. In addition, there is also a form in which a tungsten element is added at the time of synthesis of a substance capable of occluding and releasing charge transport ions, and firing is performed, so that a compound containing a tungsten element is supported on the particle surface of the positive active material or contained inside the particle. As the positive active material containing a tungsten element, a commercially available product may be used.

[0037] As the substance capable of occluding and releasing charge transport ions, a substance capable of occluding and releasing lithium ions is preferable, and conventionally known materials can be used as these substances. Examples of such a substance include lithium-transition metal composite oxides that have an α-$NaFeO_2$-type crystal structure, lithium-transition metal oxides that have a spinel-type crystal structure, polyanion compounds, chalcogenides, and sulfur. Examples of the lithium-transition metal composite oxides that have an α-$NaFeO_2$-type crystal structure include $Li[Li_xNi_{(1-x)}]O_2$ $(0 \leq x < 0.5)$, $Li[Li_xNiCo_{(1-x-\gamma)}]O_2$ $(0 \leq x < 0.5, 0 < \gamma < 1, 0 < 1 - x - \gamma)$, $Li[Li_xCo_{(1-x)}]O_2$ $(0 \leq x < 0.5)$, $Li[Li_xNi_\gamma Mn_{(1-x-\gamma)}]O_2$ $(0 \leq x < 0.5, 0 < \gamma < 1, 0 < 1 - x - \gamma)$, $Li[Li_xNi_\gamma Mn_\beta Co_{(1-x-\gamma-\beta)})]O_2$ $(0 \leq x < 0.5, 0 < \gamma, 0 < \beta, 0.5 < \gamma + \beta < 1, 0 < 1- x - \gamma < \beta)$, and $Li[Li_xNi_\gamma Co_\beta Al_{(1-x-\gamma-\beta)}]O_2$ $(0 \leq x < 0.5, 0 < \gamma, 0 < \beta, 0.5 < \gamma + \beta < 1, 0 < 1 - x - \gamma - \beta)$. Examples of the lithium-transition metal composite oxides that have a spinel-type crystal structure include $Li_xMn_2O_4$ and $Li_xNi_\gamma Mn_{(2-\gamma)}O_4$. Examples of the polyanion compounds include $LiFePO_4$, $LiMnPO_4$, $LiNiPO_4$, $LiCoPO_4$, $Li_3V_2(PO_4)_3$, Li_2MnSiO_4, and Li_2CoPO_4F. Examples of the chalcogenides include a titanium disulfide, a molybdenum disulfide, and a molybdenum dioxide. Some of atoms or polyanions in these materials may be substituted with atoms or anion species composed of other elements. One of these materials may be used alone, or two or more of these materials may be used in combination.

[0038] Among these materials, as the substance capable of occluding and releasing charge transport ions, a lithium transition metal composite oxide having an α-$NaFeO_2$-type crystal structure or a spinel-type crystal structure is preferable; a lithium transition metal composite oxide having an α-$NaFeO_2$-type crystal structure is more preferable; and $Li[Li_xNi_\gamma Mn_\beta Co_{(1-x-\gamma-\beta)})]O_2$ $(0 \leq x < 0.5, 0 < \gamma, 0 < \beta, 0.5 < \gamma + \beta < 1, 0 < 1 - x - \gamma - \beta)$ is still more preferable. In the above $Li[Li_xNi_\gamma Mn_\beta Co_{(1-x-\gamma-\beta)}]O_2$, for example, $0.1 \leq \gamma < 0.9$ and $0.1 \leq \beta < 0.9$ are preferable. When such a substance is used, the effect of improving the input by the tungsten element is particularly sufficiently exhibited.

[0039] The positive active material preferably further contains a transition metal element other than the tungsten element. When a lithium transition metal composite oxide, a polyanion compound, or the like is used as the substance capable of occluding and releasing charge transport ions, the positive active material further contains a transition metal element other than the tungsten element. The content of the tungsten element with respect to all transition metal elements other than the tungsten element in the positive active material is preferably 0.2 mol% or more and 3 mol% or less, and more preferably 0.5 mol% or more and 2 mol% or less. By setting the content of the tungsten element to the above lower limit or more, the effect of the tungsten element in the positive active material is sufficiently exhibited, and the input at the initial stage and after storage in a high temperature environment further increases. On the other hand, by setting the content of the tungsten element to the above upper limit or less, the ion conductivity of the positive active material is enhanced, and as a result, the input at the initial stage and after storage in a high temperature environment further increases.

[0040] The content of the positive active material in the positive active material layer is preferably 50% by mass or more and 99% by mass or less, more preferably 70% by mass or more and 98% by mass or less, and still more preferably 80% by mass or more and 95% by mass or less. When the content of the positive active material falls within the range mentioned above, a balance can be achieved between the high energy density and productivity of the positive active material layer.

[0041] The positive active material is typically particles (powder). The average particle size of the positive active material is preferably 0.1 pm or more and 20 pm or less, for example. When the average particle size of the positive active material is equal to or more than the lower limit mentioned above, the positive active material is easily manufactured or handled. When the average particle size of the positive active material is equal to or less than the upper limit mentioned above, the electron conductivity of the positive active material layer is improved. It is to be noted that in the case of using a composite of the positive active material and another material, the average particle size of the composite is regarded as the average particle size of the positive active material.

[0042] A crusher, a classifier, or the like is used in order to obtain a powder with a predetermined particle size. Examples of a crushing method include a method in which a mortar, a ball mill, a sand mill, a vibratory ball mill, a planetary ball mill, a jet mill, a counter jet mill, a whirling airflow type jet mill, or a sieve or the like is used. At the time of crushing, wet-type crushing in coexistence of water or an organic solvent such as hexane can also be used. As a classification method, a sieve or a wind force classifier or the like is used based on the necessity both in dry manner and in wet manner.

[0043] The conductive agent is not particularly limited as long as it is a material exhibiting conductivity. Examples of such a conductive agent include carbonaceous materials, metals, and conductive ceramics. Examples of the carbonaceous materials include graphite, non-graphitic carbon, and graphene-based carbon. Examples of the non-graphitic carbon include carbon nanofibers, pitch-based carbon fibers, and carbon black. Examples of the carbon black include furnace black, acetylene black, and ketjen black. Examples of the graphene-based carbon include graphene, carbon nanotubes (CNTs), and fullerene. Examples of the form of the conductive agent include a powdery form and a fibrous form. As the conductive agent, one of these materials may be used singly, or two or more thereof may be mixed and used. These materials may be composited and then used. For example, a material in which carbon black and CNT are composited may be used. Among these, carbon black is preferable from the viewpoint of electron conductivity and coatability, and in particular, acetylene black is preferable.

[0044] The content of the conductive agent in the positive active material layer is preferably 1% by mass or more and 10% by mass or less, and more preferably 3% by mass or more and 9% by mass or less. By setting the content of the conductive agent to the above range, the energy density of the secondary battery can be increased.

[0045] Examples of the binder include: thermoplastic resins such as fluororesin (polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), etc.), polyethylene, polypropylene, polyacryl, and polyimide; elastomers such as an ethylene-propylene-diene rubber (EPDM), sulfonated EPDM, a styrene butadiene rubber (SBR), and a fluororubber; and polysaccharide polymers.

[0046] The content of the binder in the positive active material layer is preferably 0.5% by mass or more and 10% by mass or less, and more preferably 1% by mass or more and 9% by mass or less. By setting the content of the binder in the above range, the active material can be stably held.

[0047] Examples of the thickener include polysaccharide polymers such as carboxymethylcellulose (CMC) and methylcellulose. When the thickener has a functional group that is reactive with lithium and the like, the functional group may be deactivated by methylation or the like in advance.

[0048] The content of the thickener in the positive active material layer may be, for example, 0.1% by mass or more and 6% by mass or less, or may be 0.5% by mass or more and 3% by mass or less. The content of the thickener in the positive active material layer may be 1% by mass or less, and the positive active material layer may not contain the thickener.

[0049] The filler is not particularly limited. Examples of the filler include polyolefins such as polypropylene and polyethylene, inorganic oxides such as silicon dioxide, alumina, titanium dioxide, calcium oxide, strontium oxide, barium oxide, magnesium oxide and aluminosilicate, hydroxides such as magnesium hydroxide, calcium hydroxide and aluminum hydroxide, carbonates such as calcium carbonate, hardly soluble ionic crystals of calcium fluoride, barium fluoride, and barium sulfate, nitrides such as aluminum nitride and silicon nitride, and substances derived from mineral resources, such as talc, montmorillonite, boehmite, zeolite, apatite, kaolin, mullite, spinel, olivine, sericite, bentonite and mica, or artificial products thereof.

[0050] The content of the filler in the positive active material layer may be, for example, 0.1% by mass or more and 8% by mass or less, or may be 0.5% by mass or more and 5% by mass or less. The content of the filler in the positive active material layer may be 3% by mass or less, or may be 1% by mass or less, and the filler may not be contained in the positive active material layer.

[0051] The positive active material layer may contain typical nonmetal elements such as B, N, P, F, Cl, Br, and I, typical metal elements such as Li, Na, Mg, Al, K, Ca, Zn, Ga, Ge, Sn, Sr, and Ba, and transition metal elements such as Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Zr, and Nb as a component other than the positive active material, the conductive agent, the binder, the thickener, and the filler.

[0052] The mass per unit area of the positive active material layer is not particularly limited, but is, for example, 4.0

mg/cm^2 or more and 15 mg/cm^2 or less. The lower limit of the mass per unit area of the positive active material layer is preferably 4.5 mg/cm^2, and more preferably 4.8 mg/cm^2 or 5.0 mg/cm^2. In some aspects, the mass per unit area of the positive active material layer may be, for example, 5.5 mg/cm^2 or more, or 5.8 mg/cm^2 or more. The upper limit of the mass per unit area of the positive active material layer is preferably 12 mg/cm^2, and more preferably 10 mg/cm^2. In the nonaqueous electrolyte energy storage device including the positive active material layer in which the mass per unit area is in the above range, the effect of application of the present configuration can be more suitably exhibited. Here, "the mass per unit area of the positive active material layer" refers to a mass per unit area of one positive active material layer. For example, when the positive electrode has a positive substrate with the positive active material layer provided on each of both surfaces of the positive substrate, "the mass per unit area of the positive active material layer" is a mass per unit area of the positive active material layer on one of the surfaces. The same applies to "the mass per unit area of the negative active material layer" described later.

(Negative electrode)

[0053] The negative electrode has a negative substrate and a negative active material layer disposed directly on the negative substrate or over the negative substrate with an intermediate layer interposed therebetween. The configuration of the intermediate layer is not particularly limited, and for example, can be selected from the configurations exemplified for the positive electrode.

[0054] The negative substrate has conductivity. As the material of the negative substrate, a metal such as copper, nickel, stainless steel or a nickel-plated steel, an alloy thereof, a carbonaceous material, or the like is used. Among these metals and alloys, the copper or copper alloy is preferable. Examples of the negative substrate include a foil, a deposited film, a mesh, and a porous material, and a foil is preferable from the viewpoint of cost. Accordingly, the negative substrate is preferably a copper foil or a copper alloy foil. Examples of the copper foil include a rolled copper foil and an electrolytic copper foil.

[0055] The average thickness of the negative substrate is preferably 2 pm or more and 35 pm or less, more preferably 3 pm or more and 30 pm or less, still more preferably 4 pm or more and 25 pm or less, and particularly preferably 5 pm or more and 20 pm or less. The average thickness of the negative substrate falls within the range mentioned above, thereby allowing the energy density per volume of the secondary battery to be increased while increasing the strength of the negative substrate.

[0056] The negative active material layer contains a negative active material. The negative active material layer includes optional components such as a conductive agent, a binder, a thickener, and a filler, if necessary.

[0057] The negative active material layer may contain typical nonmetal elements such as B, N, P, F, Cl, Br, and I, typical metal elements such as Li, Na, Mg, Al, K, Ca, Zn, Ga, Ge, Sn, Sr, and Ba, and transition metal elements such as Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Zr, Ta, Hf, Nb, and W as a component other than the negative active material, the conductive agent, the binder, the thickener, and the filler.

[0058] The negative active material includes solid graphite. The negative active material contains solid graphite, whereby the input after storage in a high temperature environment is also large. The above-mentioned ratio of the area of voids (porosity) in the particles to the total area of the particles in the cross section of the solid graphite, observed in the SEM image, is 2% or less, preferably 1% or less, and more preferably 0.5% or less. The lower limit of the ratio of the area (porosity) may be 0%.

[0059] The solid graphite may be natural graphite or artificial graphite, but is preferably natural graphite. The solid graphite is natural graphite (solid natural graphite), whereby the discharge capacity per mass of the negative active material increases, and the input at the initial stage and after storage in a high temperature environment also further increases.

[0060] The natural graphite is a generic term for graphite obtained from natural resources. The shape of the solid natural graphite is not particularly limited, and examples thereof include scale-like graphite, massive graphite (flake graphite), and earthy graphite. The solid natural graphite may be spheroidized natural graphite particles obtained by spheroidizing scale-like natural graphite or the like. The natural graphite may have four peaks appearing at diffraction angles 2θ in the range from 40° to 50° in an X-ray diffraction pattern obtained with the use of $CuK\alpha$, measured before charge-discharge or in a discharged state. These four peaks are considered to be two peaks derived from a hexagonal structure and two peaks derived from a rhombohedral structure. In the case of artificial graphite, generally, only two peaks derived from a hexagonal structure are considered to appear. In the X-ray diffraction pattern, the ratio ((012)/(100)) of the peak intensity derived from the (012) plane to the peak intensity derived from the (100) plane is preferably 0.3 or more, and more preferably 0.4 or more. The ratio of the peak intensities ((012)/(100)) is preferably 0.6 or less. In this regard, the (100) plane is derived from the hexagonal structure, and the (012) plane is derived from the rhombohedral structure.

[0061] The average particle size of the solid graphite can be, for example, 1 pm or more and 25 pm or less, and is preferably 3 pm or more and 20 pm or less, more preferably 5 pm or more and 15 pm or less, and still more preferably 7 pm or more and 13 pm or less. In some aspects, the average particle size of the solid graphite may be 8 pm or more and 12 pm or less, or 9 pm or more. The average particle size of the solid graphite falls within the range mentioned above, thereby allowing the charge-discharge performance of the nonaqueous electrolyte energy storage device to be enhanced. In particular, when the average particle size of the solid graphite is the above lower limit or more, the input after storage in a high temperature environment further increases. A crusher, a classifier, or the like is used in order to obtain solid graphite with a predetermined particle size. The crushing method and classification method can be selected from, for example, the methods exemplified for the positive electrode.

[0062] The content of the solid graphite in the negative active material layer is preferably 60% by mass or more and 99.5% by mass or less, and more preferably 90% by mass or more and 99% by mass or less. By setting the content of the solid graphite in the above range, it is possible to achieve both high energy density and productivity of the negative active material layer, and it is possible to further increase the input after storage in a high temperature environment.

[0063] The negative active material may include other negative active materials besides the solid graphite. As other negative active materials, hollow graphite (graphite other than solid graphite) and other various conventionally known negative active materials can be used. However, solid graphite is preferably the main active material. For example, in a cross-sectional SEM image of the negative electrode, the ratio of the area occupied by the solid graphite to the area occupied by the negative active material (the area occupied by the solid graphite/the area occupied by the negative active material) is preferably 90% or more, and more preferably 99% or more, and may be substantially 100%. The cross-sectional SEM image of the negative electrode is acquired in the same procedure as the SEM image when "the ratio of the area of voids (porosity) in the particles to the total area of the particles" in the graphite particle is determined. The area occupied by the negative active material is the total area of the particles of the negative active material (the area also including voids). Using a cross-sectional SEM image including 10 or more particles of the negative active material in one field of view, the ratio of the area occupied by the solid graphite to the area occupied by the negative active material (the area occupied by the solid graphite/the area occupied by the negative active material) is determined. Also, the content of solid graphite in all of the negative active materials included in the negative active material layer is, however, preferably 90% by mass or more, and more preferably 99% by mass or more, and may be substantially 100% by mass. That is, it is particularly preferable that only solid graphite is used as the negative active material. As described above, by mainly using solid graphite as the negative active material, the input after storage in a high temperature environment further increases.

[0064] The content of all of the negative active materials in the negative active material layer is preferably 60% by mass or more and 99.5% by mass or less, and more preferably 90% by mass or more and 99% by mass or less. When the content of all of the negative active materials falls within the range mentioned above, a balance can be achieved between the increased energy density and manufacturability of the negative active material layer.

[0065] The conductive agent, the binder, the thickener, the filler, and the like, which are optional components in the negative active material layer, can be selected from the materials exemplified for the positive electrode. However, the graphite contained in the negative active material layer is not contained in the conductive agent.

[0066] The content of the conductive agent in the negative active material layer may be 3% by mass or less or 1% by mass or less, and the conductive agent may not be contained in the negative active material layer.

[0067] The content of the binder in the negative active material layer is preferably 0.5% by mass or more and 5% by mass or less, and more preferably 0.8% by mass or more and 3% by mass or less.

[0068] The content of the thickener in the negative active material layer is, for example, preferably 0.1% by mass or more and 6% by mass or less, and more preferably 0.5% by mass or more and 3% by mass or less.

[0069] The content of the filler in the negative active material layer may be, for example, 0.1% by mass or more and 8% by mass or less, or may be 0.5% by mass or more and 5% by mass or less. The content of the filler in the negative active material layer may be 3% by mass or less, or may be 1% by mass or less, and the filler may not be contained in the negative active material layer.

[0070] The negative active material layer can have a porosity of, for example, 30% or more and 60% or less. The lower limit of the porosity is preferably 35%, more preferably 38%, still more preferably 40%, and yet still more preferably 42%. By setting the porosity of the negative active material layer to the above lower limit or more, the input of the nonaqueous electrolyte energy storage device, particularly, the input after storage in a high temperature environment, can be further increased. On the other hand, the upper limit of the porosity is preferably 55%, more preferably 50%, and still more preferably 48%. The porosity of the negative active material layer can be adjusted by the particle size of solid graphite, the presence or absence of pressing during production, the pressure of pressing, and the like.

[0071] The mass per unit area of the negative active material layer is not particularly limited, but is, for example, 2.0 mg/cm^2 or more and 12 mg/cm^2 or less. The lower limit of the mass per unit area of the negative active material layer is preferably 2.2 mg/cm^2, and more preferably 2.5 mg/cm^2 or 2.8 mg/cm^2. In some aspects, the mass per unit area of the negative active material layer may be, for example, 3.0 mg/cm^2 or more, or 3.5 mg/cm^2 or more. The upper limit of the mass per unit area of the negative active material layer is preferably 10 mg/cm^2, and more preferably 8.0 mg/cm^2 or 6.0 mg/cm^2. In the nonaqueous electrolyte energy storage device including the negative active material layer in which the mass per unit area is in the above range, the effect of application of the present configuration can be more suitably exhibited.

[0072] Although not particularly limited, the lower limit of the ratio of the mass of solid graphite per unit area contained in the negative active material layer to the mass of tungsten element per unit area contained in the positive active material layer may be about 25. The lower limit of the ratio is preferably 30, and more preferably 32, 34, or 36 in some cases. On the other hand, the upper limit of the ratio is preferably 100, and more preferably 80, 70, 60, or 45 in some cases. In the nonaqueous electrolyte energy storage device in which the ratio is in the above range, the effect of application of the present configuration can be more suitably exhibited. The ratio of the mass of solid graphite per unit area contained in the negative active material layer to the mass of tungsten element per unit area contained in the positive active material layer can be adjusted by the content of the tungsten element in the positive active material, the content of the solid graphite in the negative active material, the mass per unit area (coating mass) of the positive active material layer and the negative active material layer, and the like.

(Separator)

[0073] The separator can be appropriately selected from known separators. As the separator, for example, a separator composed of only a substrate layer, a separator in which a heat resistant layer containing heat resistant particles and a binder is formed on one surface or both surfaces of the substrate layer, or the like can be used. Examples of the form of the substrate layer of the separator include a woven fabric, a nonwoven fabric, and a porous resin film. Among these forms, a porous resin film is preferable from the viewpoint of strength, and a nonwoven fabric is preferable from the viewpoint of liquid retaining properties of the nonaqueous electrolyte. As the material for the substrate layer of the separator, for example, a polyolefin such as polyethylene or polypropylene is preferable from the viewpoint of shutdown function, and polyimide, aramid, or the like is preferable from the viewpoint of resistance to oxidative decomposition. As the substrate layer of the separator, a material obtained by combining these resins may be used.

[0074] The heat resistant particles contained in the heat resistant layer preferably have a mass loss of 5% or less when the temperature is raised from room temperature to 500°C in an air atmosphere at 1 atm, and more preferably have a mass loss of 5% or less when the temperature is raised from room temperature to 800°C. Examples of materials that have a mass loss equal to or less than a predetermined value include inorganic compounds. Examples of the inorganic compound include oxides such as iron oxide, silicon oxide, aluminum oxide, titanium dioxide, zirconium oxide, calcium oxide, strontium oxide, barium oxide, magnesium oxide and aluminosilicate; nitrides such as aluminum nitride and silicon nitride; carbonates such as calcium carbonate; sulfates such as barium sulfate; hardly soluble ionic crystals such as calcium fluoride, barium fluoride, barium titanate; covalently bonded crystals such as silicon and diamond; and substances derived from mineral resources, such as talc, montmorillonite, boehmite, zeolite, apatite, kaolin, mullite, spinel, olivine, sericite, bentonite, and mica, and artificial products thereof. As the inorganic compounds, a simple substance or a complex of these substances may be used singly, or two or more thereof may be used in mixture. Among these inorganic compounds, silicon oxide, aluminum oxide, or aluminosilicate is preferable from the viewpoint of safety of the energy storage device.

[0075] The porosity of the separator is preferably 80% by volume or less from the viewpoint of strength, and is preferably 20% by volume or more from the viewpoint of discharge performance. The "porosity" herein is a volume-based value, which means a value measured with a mercury porosimeter.

[0076] As the separator, a polymer gel containing a polymer and a nonaqueous electrolyte may be used. Examples of the polymer include polyacrylonitrile, polyethylene oxide, polypropylene oxide, polymethyl methacrylate, polyvinyl acetate, polyvinylpyrrolidone, and polyvinylidene fluoride. The use of the polymer gel has the effect of suppressing liquid leakage. As the separator, the polymer gel may be used concurrently with a porous resin film, a nonwoven fabric, or the like as described above.

(Nonaqueous electrolyte)

[0077] The nonaqueous electrolyte can be appropriately selected from known nonaqueous electrolytes. For the nonaqueous electrolyte, a nonaqueous electrolyte solution may be used. The nonaqueous electrolyte solution includes a nonaqueous solvent and an electrolyte salt dissolved in the nonaqueous solvent.

[0078] The nonaqueous solvent can be appropriately selected from known nonaqueous solvents. Examples of the nonaqueous solvent include cyclic carbonates, chain carbonates, carboxylic acid esters, phosphoric acid esters, sulfonic acid esters, ethers, amides, and nitriles. As the nonaqueous solvent, solvents in which some hydrogen atoms contained in these compounds are substituted with halogen may be used.

[0079] Examples of the cyclic carbonates include ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), vinylene carbonate (VC), vinylethylene carbonate (VEC), chloroethylene carbonate, fluoroethylene carbonate (FEC), difluoroethylene carbonate (DFEC), styrene carbonate, 1-phenylvinylene carbonate, and 1,2-diphenylvinylene carbonate. Among these carbonates, EC is preferable.

[0080] Examples of the chain carbonates include diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diphenyl carbonate, trifluoroethyl methyl carbonate, and bis(trifluoroethyl)carbonate. Among these carbonates, EMC is preferable.

[0081] As the nonaqueous solvent, it is preferable to use the cyclic carbonate or the chain carbonate, and it is more preferable to use the cyclic carbonate and the chain carbonate in combination. The use of the cyclic carbonate allows the promoted dissociation of the electrolyte salt to improve the ionic conductivity of the nonaqueous electrolyte solution. The use of the chain carbonate allows the viscosity of the nonaqueous electrolyte solution to be kept low. In a case where a cyclic carbonate and a chain carbonate are used in combination, a volume ratio of the cyclic carbonate to the chain carbonate (cyclic carbonate : chain carbonate) is preferably in a range from 5 : 95 to 50 : 50, for example.

[0082] The electrolyte salt can be appropriately selected from known electrolyte salts. Examples of the electrolyte salt include a lithium salt, a sodium salt, a potassium salt, a magnesium salt, and an onium salt. Among these, a lithium salt is preferable.

[0083] Examples of the lithium salt include inorganic lithium salts such as LiPFs, $LiPO_2F_2$, $LiBF_4$, $LiClO_4$, and $LiN(SO_2F)_2$, lithium oxalates such as lithium bis(oxalate)borate (LiBOB), lithium difluorooxalatoborate (LiFOB), and lithium bis(oxalate)difluorophosphate (LiFOP), and lithium salts having a halogenated hydrocarbon group, such as $LiSO_3CF_3$, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiN(SO_2CF_3)(SO_2C_4F_9)$, $LiC(SO_2CF_3)_3$, and $LiC(SO_2C_2F_5)_3$. Among these, inorganic lithium salts are preferable, and $LiPF_6$ is more preferable.

[0084] When $LiPF_6$ is contained in the nonaqueous electrolyte solution, it is easy to generate HF by reacting $LiPF_6$ with water slightly present in the nonaqueous electrolyte solution. It is considered that the presence of HF in the nonaqueous electrolyte solution promotes elution of tungsten element from the positive active material into the nonaqueous electrolyte solution. In addition, when an electrolyte salt having an anion containing a fluorine element, an oxygen element, and a phosphorus element, such as $LiPO_2F_2$ and lithium bis(oxalate)difluorophosphate (LiFOP), is present in the nonaqueous electrolyte solution, it is considered that elution of the tungsten element from the positive active material into the nonaqueous electrolyte is further promoted. Therefore, when the nonaqueous electrolyte energy storage device using the nonaqueous electrolyte solution containing such a component is one embodiment of the present invention, the effect of increasing the input after storage in a high temperature environment is particularly remarkable. The content of the electrolyte salt having an anion containing a fluorine element, an oxygen element, and a phosphorus element in the nonaqueous electrolyte solution may be, at 20°C and 1 atm, for example, 0.01 mol/dm^3 or more and 0.5 mol/dm^3 or less, 0.03 mol/dm^3 or more and 0.3 mol/dm^3 or less, or 0.05 mol/dm^3 or more and 0.2 mol/dm^3 or less.

[0085] The content of the electrolyte salt in the nonaqueous electrolyte solution is, at 20°C and 1 atm, preferably 0.1 mol/dm^3 or more and 2.5 mol/dm^3 or less, more preferably 0.3 mol/dm^3 or more and 2.0 mol/dm^3 or less, still more preferably 0.5 mol/dm^3 or more and 1.7 mol/dm^3 or less, and particularly preferably 0.7 mol/dm^3 or more and 1.5 mol/dm^3 or less. The content of the electrolyte salt falls within the range mentioned above, thereby allowing the ionic conductivity of the nonaqueous electrolyte solution to be increased.

[0086] The nonaqueous electrolyte solution may include an additive, besides the nonaqueous solvent and the electrolyte salt. Examples of the additive include aromatic compounds such as biphenyl, alkylbiphenyl, terphenyl, partly hydrogenated terphenyl, cyclohexylbenzene, t-butylbenzene, t-amylbenzene, diphenyl ether, and dibenzofuran; partial halides of the aromatic compounds such as 2-fluorobiphenyl, o-cyclohexylfluorobenzene, and p-cyclohexylfluorobenzene; halogenated anisole compounds such as 2,4-difluoroanisole, 2,5-difluoroanisole, 2,6-difluoroanisole, and 3,5-difluoroanisole; vinylene carbonate, methylvinylene carbonate, ethylvinylene carbonate, succinic anhydride, glutaric anhydride, maleic anhydride, citraconic anhydride, glutaconic anhydride, itaconic anhydride, cyclohexanedicarboxylic anhydride; ethylene sulfite, propylene sulfite, dimethyl sulfite, methyl methanesulfonate, busulfan, methyl toluenesulfonate, dimethyl sulfate, ethylene sulfate, sulfolane, dimethyl sulfone, diethyl sulfone, dimethylsulfoxide, diethyl sulfoxide, tetramethylene sulfoxide, diphenyl sulfide, 4,4'-bis(2,2-dioxo-1,3,2-dioxathiolane, 4-methylsulfonyloxymethyl-2,2-dioxo-1,3,2-dioxathiolane, thioanisole, diphenyl disulfide, dipyridinium disulfide, 1,3-propene sultone, 1,3-propane sultone, 1,4-butane sultone, 1,4-butene sultone, perfluorooctane, tristrimethylsilyl borate, tristrimethylsilyl phosphate, and tetrakistrimethylsilyl titanate. These additives may be used singly, or in mixture of two or more thereof.

[0087] The content of the additive contained in the nonaqueous electrolyte solution is preferably 0.01% by mass or more and 10% by mass or less, more preferably 0.1% by mass or more and 7% by mass or less, still more preferably 0.2% by mass or more and 5% by mass or less, and particularly preferably 0.3% by mass or more and 3% by mass or less, with respect to the total mass of the nonaqueous electrolyte solution. When the content of the additive falls within the above range, thereby making it possible to improve capacity retention performance or cycle performance after high-temperature storage, and to further improve safety.

[0088] As the nonaqueous electrolyte, a solid electrolyte may be used, or a nonaqueous electrolyte solution and a solid electrolyte may be used in combination.

[0089] The solid electrolyte can be selected from any material with ionic conductivity, which is solid at normal temperature (for example, 15°C to 25°C), such as lithium, sodium and calcium. Examples of the solid electrolyte include sulfide solid electrolytes, oxide solid electrolytes, nitride solid electrolytes, and polymer solid electrolytes.

[0090] Examples of the lithium ion secondary battery include $Li_2S-P_2S_5$, $LiI-Li_2S-P_2S_5$, and $Li_{10}Ge-P_2S_{12}$ as the sulfide solid electrolyte.

[0091] The shape of the nonaqueous electrolyte energy storage device according to the present embodiment is not particularly limited, and examples thereof include cylindrical batteries, prismatic batteries, flat batteries, coin batteries, and button batteries.

[0092] Fig. 1 illustrates a nonaqueous electrolyte energy storage device 1 as an example of prismatic batteries. It is to be noted that Fig. 1 is a view illustrating the inside of a case in a perspective manner. An electrode assembly 2 including a positive electrode and a negative electrode wound with a separator interposed therebetween is housed in a prismatic case 3. The positive electrode is electrically connected to a positive electrode terminal 4 via a positive electrode lead 41. The negative electrode is electrically connected to a negative electrode terminal 5 via a negative electrode lead 51.

<Energy storage apparatus>

[0093] The nonaqueous electrolyte energy storage device according to the present embodiment can be mounted as an energy storage unit (battery module) configured by assembling a plurality of nonaqueous electrolyte energy storage devices on a power source for automobiles such as electric vehicles (EV), hybrid vehicles (HEV), and plug-in hybrid vehicles (PHEV), a power source for electronic devices such as personal computers and communication terminals, or a power source for power storage, or the like. In this case, the technique of the present invention may be applied to at least one nonaqueous electrolyte energy storage device included in the energy storage unit.

[0094] Fig. 2 shows an example of an energy storage apparatus 30 formed by assembling energy storage units 20 in each of which two or more electrically connected nonaqueous electrolyte energy storage devices 1 are assembled. The energy storage apparatus 30 may include a busbar (not illustrated) for electrically connecting two or more nonaqueous electrolyte energy storage devices 1 and a busbar (not illustrated) for electrically connecting two or more energy storage units 20. The energy storage unit 20 or the energy storage apparatus 30 may include a state monitor (not illustrated) that monitors the state of one or more nonaqueous electrolyte energy storage devices.

<Method for manufacturing nonaqueous electrolyte energy storage device>

[0095] A method for manufacturing the nonaqueous electrolyte energy storage device according to the present embodiment can be appropriately selected from publicly known methods. The manufacturing method includes, for example, preparing an electrode assembly, preparing a nonaqueous electrolyte, and housing the electrode assembly and the nonaqueous electrolyte in a case. Preparing the electrode assembly includes: preparing a positive electrode and a negative electrode, and forming an electrode assembly by stacking or winding the positive electrode and the negative electrode with a separator interposed therebetween.

[0096] The positive electrode can be prepared, for example, by applying a positive composite paste to a positive substrate directly or via an intermediate layer, followed by drying. The positive composite paste contains components constituting a positive active material layer such as a positive active material, and a dispersion medium. The applied positive composite paste may be dried and then pressed or the like.

[0097] The negative electrode can be prepared, for example, by applying a negative composite paste to a negative substrate directly or via an intermediate layer, followed by drying. The negative composite paste contains components constituting the negative active material layer, such as solid graphite, and a dispersion medium. The applied negative composite paste may be dried and then pressed or the like. The porosity of the negative active material layer to be formed can be adjusted by the presence or absence of pressing, the pressure of pressing, and the like.

[0098] Housing the nonaqueous electrolyte in a case can be appropriately selected from known methods. For example, in the case of using a nonaqueous electrolyte solution for the nonaqueous electrolyte, the nonaqueous electrolyte solution may be injected from an inlet formed in the case, and the inlet may be then sealed.

<Other embodiments>

[0099] The nonaqueous electrolyte energy storage device according to the present invention is not limited to the embodiment described above, and various changes may be made without departing from the gist of the present invention. For example, to the configuration of an embodiment, the configuration of another embodiment can be added, and a part of the configuration of an embodiment can be replaced by the configuration of another embodiment or a well-known technique. Furthermore, a part of the configuration according to one embodiment can be deleted. In addition, a well-known technique can be added to the configuration according to one embodiment.

[0100] While a case where the nonaqueous electrolyte energy storage device is used as a nonaqueous electrolyte secondary battery (lithium ion secondary battery) that is chargeable and dischargeable has been described in the embodiment mentioned above, the type, shape, dimensions, capacity, and the like of the nonaqueous electrolyte energy storage device are arbitrary. The present invention can also be applied to various secondary batteries, and capacitors such as electric double layer capacitors and lithium ion capacitors.

[0101] While the electrode assembly with the positive electrode and the negative electrode stacked with the separator interposed therebetween has been described in the embodiment mentioned above, the electrode assembly may include no separator. For example, the positive electrode and the negative electrode may be brought into direct contact with each other, with a non-conductive layer formed on the active material layer of the positive electrode or negative electrode.

EXAMPLES

[0102] Hereinafter, the present invention will be described in more detail with reference to Examples, but the present invention is not limited to the following Examples.

[Example 1]

(Fabrication of positive electrode)

[0103] A positive active material was prepared in which tungsten oxide was deposited on the particle surface of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. The content of the tungsten element with respect to a transition metal element other than the tungsten element in the positive active material was 1 mol%.

[0104] A positive composite paste was prepared using the positive active material, acetylene black (AB) as a conductive agent, a polyvinylidene fluoride (PVDF) as a binder, and an N-methylpyrrolidone (NMP) as a dispersion medium. It is to be noted that the mass ratios of the positive active material, AB, and PVDF were set to be 93 : 5 : 2 (in terms of solid content). The positive composite paste was applied to both surfaces of an aluminum foil as a positive substrate such that the applied mass (mass of the solid content) was 6 mg/cm^2, and dried. Thereafter, roll pressing was performed to obtain a positive electrode with the positive active material layer stacked on both surfaces of the positive electrode substrate.

(Fabrication of negative electrode)

[0105] Solid graphite (solid naturel graphite, porosity: 0.45%, average particle size: 9.9 pm) as a negative active material, a styrene-butadiene rubber (SBR) as a binder, carboxymethyl cellulose (CMC) as a thickener, and water as a dispersion medium were used to prepare a negative composite paste. It is to be noted that the mass ratios of solid graphite, SBR, and CMC were set to be 98.5 : 1 : 0.5 (in terms of solid content). The negative composite paste was applied to both surfaces of a copper foil as a negative substrate such that the applied mass (mass of the solid content) was 4 mg/cm^2, and dried. Thereafter, roll pressing was performed to obtain a negative electrode with the negative active material layer stacked on both surfaces of the negative substrate. The negative active material layer had a porosity of 45%.

(Nonaqueous electrolyte solution)

[0106] LiPFs was dissolved at a concentration of 1.2 mol/dm^3 in a solvent obtained by mixing an ethylene carbonate and an ethyl methyl carbonate at a volume ratio of 30 : 70 and $LiPO_2F_2$ was dissolved at a concentration of 1% by mass to obtain a nonaqueous electrolyte solution.

(Separator)

[0107] A polyolefin microporous membrane was used for the separator.

(Assembly of nonaqueous electrolyte energy storage device)

[0108] The positive electrode, the negative electrode, and the separator were used to obtain a wound electrode assembly. The electrode assembly was housed in a case, the nonaqueous electrolyte solution was injected into the case, and the case was sealed to obtain a nonaqueous electrolyte energy storage device according to Example 1.

[Examples 2 to 4, Comparative Examples 1 to 3]

[0109] Nonaqueous electrolyte energy storage devices of Examples 2 to 4 and Comparative Examples 1 to 3 were obtained similarly to Example 1 except that the types of the positive active material and the negative active material and the porosity of the negative active material layer were as shown in Tables 1 and 2.

[0110] "Presence" in the column of "Presence or absence of positive active material W (tungsten element)" in Tables 1 and 2 indicates the positive active material used in Example 1 described above, and "Absence" indicates $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ containing no tungsten element. "Hollow graphite" indicates hollow natural graphite having a porosity of 3% and an average particle size of 9.1 pm. The porosity of the negative active material layer was adjusted by changing the pressure during pressing. Also, Example 1 is described in both Table 1 and Table 2.

[Evaluation]

(1-1) Initial charge-discharge

[0111] The obtained respective nonaqueous electrolyte energy storage devices were subjected to the initial charge-discharge under the following conditions. In a thermostatic chamber at 25°C, the nonaqueous electrolyte energy storage devices were subjected to constant current charge at a charge current of 1.0 C and an end-of-charge voltage of 4.10 V, and then to constant voltage charge at 4.10 V. With regard to the charge termination conditions, the charge was performed until the total charge time reached 3 hours. Thereafter, a pause of 10 minutes was provided. The energy storage devices were subjected to constant current discharge at a discharge current of 1.0 C and an end-of-discharge voltage of 3.0 V.

(1-2) Measurement of initial input

[0112] The respective nonaqueous electrolyte energy storage device after the initial charge-discharge were subjected to constant current charge at a charge current of 1.0 C in a thermostatic chamber at 25°C to adjust the SOC to 50%, stored in a thermostatic chamber at -30°C for 4 hours, and then charged at a constant current of 5 C, 10 C, 15 C, 20 C, or 25 C for 10 seconds. After completion of each charge, constant current discharge was performed at a current of 1.0 C to set the SOC to 50%. The resistance value was calculated from the slope of the current in each charge and the voltage 1 second after the start of charge, and "{difference between voltage before charge and upper limit voltage (4.3 V)}/resistance value × upper limit voltage (4.3 V)" was determined, and used as an initial input. The input is energy (power) that can be taken in per unit time.

(1-3) Measurement of input after storage in high temperature environment

[0113] Subsequently, the respective nonaqueous electrolyte energy storage devices were each subjected to constant current constant voltage charge at a charge current of 1.0 C in a thermostatic chamber at 25°C to set the SOC of 80%. The respective nonaqueous electrolyte energy storage devices were stored in a thermostatic chamber at 80°C for 10 days in the state of SOC of 80%. Thereafter, the respective nonaqueous electrolyte energy storage devices were stored in a thermostatic chamber at 25°C for 3 hours or more, and subjected to constant current discharge at a discharge current of 1.0 C and an end-of-discharge voltage of 3.0 V, then the input was obtained in the same manner as in the initial input, and the obtained input was used as an input after storage (input after storage in a high temperature environment).

[0114] The initial input and the input after storage in the respective nonaqueous electrolyte energy storage devices are shown in Tables 1 and 2.

[Table 1]

	Positive active material layer	Negative active material layer		Evaluation	
	Presence or absence of positive active material W	Negative active material	Porosity (%)	Initial input (W)	Input after storage (W)
Example 1	Presence	Solid graphite particle	45	130	112
Comparative Example 1		Hollow graphite particle		133	88
Comparative Example 2	Absence	Solid graphite particle		98	94
Comparative Example 3		Hollow graphite particle		99	97

[Table 2]

	Positive active material layer	Negative active material layer		Evaluation	
	Presence or absence of positive active material W	Negative active material	Porosity (%)	Initial input (W)	Input after storage (W)
Example 2	Presence	Solid graphite particle	35	126	101
Example 3			40	129	110
Example 1			45	130	112
Example 4			50	128	111

[0115] As shown in Table 1, in the respective nonaqueous electrolyte energy storage devices of Comparative Examples 2 and 3 in which the positive active material does not contain a tungsten element, the initial input is small. In the nonaqueous electrolyte energy storage device of Comparative Example 1 in which the positive active material contains a tungsten element and the negative active material is hollow graphite, the initial input is large, but the input after storage is small. On the other hand, the nonaqueous electrolyte energy storage device of Example 1 in which the positive active material contained a tungsten element and the negative active material was solid graphite had a large initial input and a large input after storage. In addition, as shown in Table 2, it is found that the input, particularly, the input after storage, tends to increase by increasing the porosity of the negative active material layer.

INDUSTRIAL APPLICABILITY

[0116] The present invention can be applied to nonaqueous electrolyte energy storage devices and the like for use as power sources for electronic devices such as personal computers and communication terminals, and automobiles and the like.

DESCRIPTION OF REFERENCE SIGNS

[0117]

1: Nonaqueous electrolyte energy storage device
2: Electrode assembly
3: Case
4: Positive electrode terminal
41: Positive electrode lead
5: Negative electrode terminal
51: Negative electrode lead
20: Energy storage unit
30: Energy storage apparatus

Claims

1. A nonaqueous electrolyte energy storage device comprising:

a positive electrode containing a positive active material containing a tungsten element; and
a negative electrode containing solid graphite.

2. The nonaqueous electrolyte energy storage device according to claim 1, wherein

the negative electrode has a negative active material layer containing the solid graphite, and
the negative active material layer has a porosity of 40% or more.

3. The nonaqueous electrolyte energy storage device according to claim 1 or 2, wherein

the positive active material further contains a transition metal element other than the tungsten element, and
a content of the tungsten element with respect to a transition metal element other than the tungsten element in the

positive active material is 0.2 mol% or more.

4. The nonaqueous electrolyte energy storage device according to claim 1 or 2, wherein the solid graphite is solid natural graphite.

5. The nonaqueous electrolyte energy storage device according to claim 1 or 2, wherein the solid graphite has an average particle size of 5 μm or more.

Fig. 1

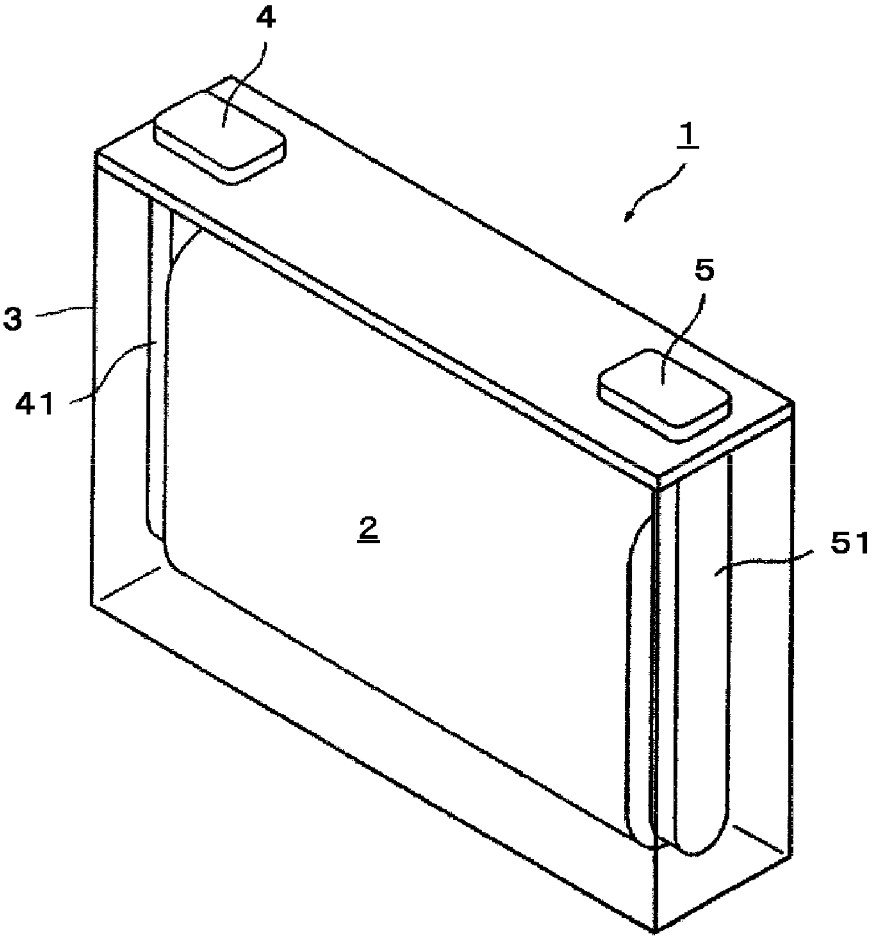
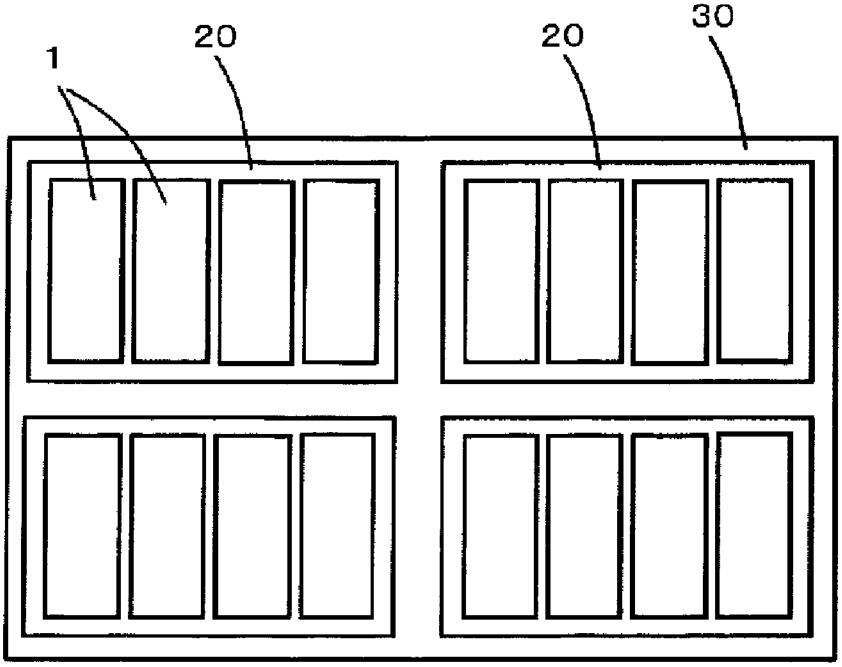


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/018450

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/058(2010.01)i; ***H01G 11/32***(2013.01)i; ***H01G 11/46***(2013.01)i; ***H01M 4/133***(2010.01)i; ***H01M 4/587***(2010.01)i; ***H01M 10/0525***(2010.01)i; *H01M 4/36*(2006.01)n; *H01M 4/505*(2010.01)n; *H01M 4/525*(2010.01)n

FI: H01M10/058; H01G11/32; H01G11/46; H01M4/133; H01M4/587; H01M10/0525; H01M4/36 C; H01M4/505; H01M4/525

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M10/058; H01G11/32; H01G11/46; H01M4/133; H01M4/587; H01M10/0525; H01M4/36; H01M4/505; H01M4/525

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2020-191224 A (GS YUASA CORP) 26 November 2020 (2020-11-26)	1-5
A	JP 2015-210891 A (TOYOTA MOTOR CORP) 24 November 2015 (2015-11-24)	1-5
A	WO 2020/144977 A1 (GS YUASA CORP) 16 July 2020 (2020-07-16)	1-5
A	WO 2020/054708 A1 (GS YUASA CORP) 19 March 2020 (2020-03-19)	1-5
A	WO 2016/157735 A1 (SANYO ELECTRIC CO., LTD.) 06 October 2016 (2016-10-06)	1-5

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search **05 July 2023**	Date of mailing of the international search report **18 July 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/018450

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